

CLAIMS

1. A composite (M) comprising:

5 - at least 75 vol% of a mixed electronic/oxygen
O²⁻ anionic conducting compound (C₁) chosen from
doped ceramic oxides which, at the use
temperature, are in the form of a crystal lattice
having oxide ion vacancies and more particularly
10 in the form of a cubic phase, fluorite phase,
aurivillius-type perovskite phase, brown-millerite
phase or pyrochlore phase; and

 - from 0.01 to 25 vol% of a compound (C₂),
different from compound (C₁), chosen from ceramics
of oxide type, ceramics of nonoxide type, metals,
15 metal alloys or mixtures of these various types of
materials; and

 - from 0 vol% to 2.5 vol% of a compound (C₃)
produced from at least one chemical reaction
represented by the equation:

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$$xF_{C1} + yF_{C2} \rightarrow zF_{C3},$$

 in which equation F_{C1}, F_{C2} and F_{C3} represent the
respective crude formulae of compounds (C₁), (C₂)
and (C₃) and x, y and z represent rational
numbers greater than or equal to 0.

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2. The composite as defined in claim 1, in which the
grains of compound (C₂) have an equiaxed shape with
a diameter ranging from 0.1 µm to 5 µm and
preferably less than 1 µm.

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3. The composite as defined in either of claims 1 and
2, in which the volume fraction of compound (C₃)
does not exceed 1.5% and more particularly does
not exceed 0.5% by volume.

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4. The composite as defined in claim 3, in which the
volume fraction of compound (C₃) in the composite
tends toward 0.

5. The composite as defined in one of claims 1 to 4, in which the volume fraction of compound (C₂) is not less than 0.1% but does not exceed 10%.
- 5 6. The composite as defined in claim 5, in which the volume fraction of compound (C₂) does not exceed 5%.
- 10 7. The composite as defined in one of claims 1 to 6, in which compound (C₂) is chosen from oxide-type materials and preferably from magnesium oxide (MgO), calcium oxide (CaO), aluminum oxide (Al₂O₃), zirconium oxide (ZrO₂), titanium oxide (TiO₂),
15 mixed strontium aluminum oxides SrAl₂O₄ or Sr₃Al₂O₆, mixed barium titanium oxide (BaTiO₃), mixed calcium titanium oxide (CaTiO₃), La_{0.5} Sr_{0.5} Fe_{0.9} Ti_{0.1} O_{3-δ} or La_{0.6} Sr_{0.4} Fe_{0.9} Ga_{0.1} O_{3-δ}.
- 20 8. The composite as defined in one of claims 1 to 6, in which compound (C₂) is chosen from materials of the nonoxide type and preferably from silicon carbide (SiC), boron nitride (BN), nickel (Ni), platinum (Pt), palladium (Pd) and rhodium (Rh).
- 25 9. The composite as defined in one of claims 1 to 8, in which compound (C₁) is chosen from oxides of formula (I):
- $$(R_aO_b)_{1-x} (R_cO_d)_x \quad (I),$$
- 30 in which:
- R_a represents at least one trivalent or tetravalent atom mainly chosen from bismuth (Bi), cerium (Ce), zirconium (Zr), thorium (Th), gallium (Ga) and hafnium (Hf), and a and b are such that
35 the structure R_aO_b is electrically neutral;
- R_c represents at least one divalent or trivalent atom chosen mainly from magnesium (Mg), calcium (Ca), barium (Ba), strontium (Sr), gadolinium (Gd), scandium (Sc), ytterbium (Yb), yttrium (Y),

10 $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ (Ia),
in which x is between 0.05 and 0.15.

$$[\text{Ma}_{1-x-u}\text{Ma}'_x\text{Ma}''_u] [\text{Mb}_{1-y-v}\text{Mb}'_y\text{Mb}''_v] \text{O}_{3-w} \quad (\text{II})$$

- Ma represents an atom chosen from scandium, yttrium, or from the families of lanthanides, actinides or alkaline-earth metals;

25 - Ma'' , which is different from Ma and Ma' ,
represents an atom chosen from aluminum (Al),
gallium (Ga), indium (In), thallium (Tl) or from
the family of alkaline-earth metals;

- Mb', which is different from Mb, represents an atom chosen from transition metals, aluminum (Al), indium (In), gallium (Ga), germanium (Ge), antimony (Sb), bismuth (Bi), tin (Sn), lead (Pb) and titanium (Ti);

- Mb", which is different from Mb and Mb', represents an atom chosen from transition metals, alkaline-earth metals, aluminum (Al), indium (In), gallium (Ga), germanium (Ge), antimony (Sb),

bismuth (Bi), tin (Sn), lead (Pb) and titanium (Ti);

$$0 < x \leq 0.5;$$

$$0 \leq u \leq 0.5;$$

5 $(x + u) \leq 0.5;$

$$0 \leq y \leq 0.9;$$

$$0 \leq v \leq 0.9;$$

$$0 \leq (y + v) \leq 0.9; \text{ and}$$

10 w is such that the structure in question is electrically neutral.

12. The composite as defined in claim 11, in which compound (C₁) is chosen from compounds of formula (IIa):

15 $\text{La}_{(1-x-u)}\text{Ma}'_x\text{Ma}''_u\text{Mb}_{(1-y-v)}\text{Mb}'_y\text{Mb}''_v\text{O}_{3-\delta}$ (IIa),
corresponding to formula (II), in which Ma represents a lanthanum atom.

13. The composite as defined in either of claims 11 and 12, in which compound (C₁) is chosen from compounds of formula (IIb):

20 $\text{Ma}_{(1-x-u)}\text{Sr}_x\text{Ma}''_u\text{Mb}_{(1-y-v)}\text{Mb}'_y\text{Mb}''_v\text{O}_{3-\delta}$ (IIb),
corresponding to formula (II) in which Ma' represents a strontium atom.

14. The composite as defined in one of claims 11 to 13, in which compound (C₁) is chosen from compounds of formula (IIc):

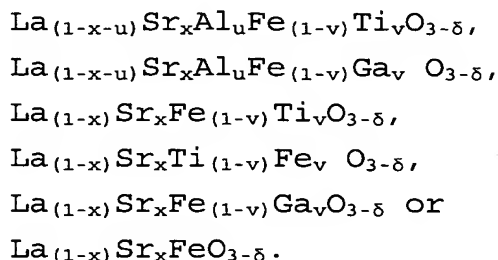
25 $\text{Ma}_{(1-x-u)}\text{Ma}'_x\text{Ma}''_u\text{Fe}_{(1-y-v)}\text{Mb}'_y\text{Mb}''_v\text{O}_{3-\delta}$ (IIc),
30 corresponding to formula (II) in which Mb represents an iron atom.

15. The composite as defined in one of claims 11 to 14, in which compound (C₁) is chosen from compounds of formula (IIId):

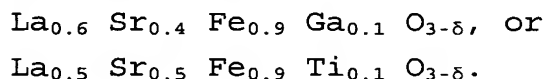
35 $\text{La}_{(1-x)}\text{Sr}_x\text{Fe}_{(1-v)}\text{Mb}''_v\text{O}_{3-\delta}$ (IIId),
corresponding to formula (II) in which $u = 0$, $y = 0$, Mb represents an iron atom, Ma represents a lanthanum atom and Ma' represents a strontium

atom.

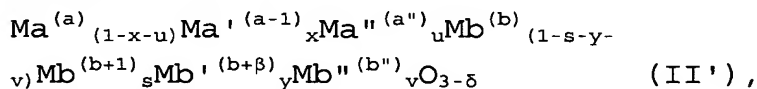
16. The composite as defined in one of claims 11 to 15, in which compound (C₁) is a compound of formula:



17. The composite as defined in claim 16, of formula:



18. The composite as defined in one of claims 11 to 17, in which compound (C₁) is chosen from those of formula (II'):



in which formula (II'):

a, a-1, a'', b, (b+1), (b+β) and b'' are integers representing the respective valences of the Ma, Ma', Ma'', Mb, Mb' and Mb'' atoms; and a, a'', b, b'', β, x, y, s, u, v and δ are such that the electrical neutrality of the crystal lattice is preserved,

$$a > 1;$$

$$a'', b \text{ and } b'' \text{ are greater than zero;}$$

$$-2 \leq \beta \leq 2;$$

$$a + b = 6;$$

$$0 < s < x;$$

$$0 < x \leq 0.5;$$

$$0 \leq u \leq 0.5;$$

$$(x + u) \leq 0.5;$$

$$0 \leq y \leq 0.9;$$

$$0 \leq v \leq 0.9;$$

$$0 \leq (y + v + s) \leq 0.9;$$

$$[u (a'' - a) + v (b'' - b) - x + s + \beta y + 2\delta] = 0;$$

and

$$\delta_{\min} < \delta < \delta_{\max} \text{ where}$$

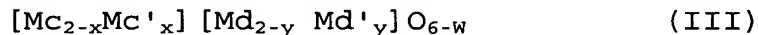
$$\delta_{\min} = [u (a - a'') + v (b - b'') - \beta y] / 2 \text{ and}$$

$$\delta_{\max} = [u (a - a'') + v (b - b'') - \beta y + x] / 2$$

and Ma, Ma', Ma'', Mb, Mb' and Mb'' are as defined above, Mb representing an atom chosen from transition metals capable of existing in several possible valences.

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19. The composite as defined in one of claims 1 to 8, in which compound (C₁) is chosen from oxides of formula (III):



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in which:

Mc represents an atom chosen from scandium, yttrium or from the families of lanthanides, actinides and alkaline-earth metals;

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Mc', which is different from Mc, represents an atom chosen from scandium, yttrium or from the families of lanthanides, actinides and alkaline-earth metals;

Md represents an atom chosen from transition metals; and

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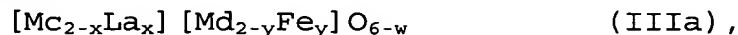
Md', which is different from Md, represents an atom chosen from transition metals, aluminum (Al), indium (In), gallium (Ga), germanium (Ge), antimony (Sb), bismuth (Bi), tin (Sn), lead (Pb) and titanium (Ti); and

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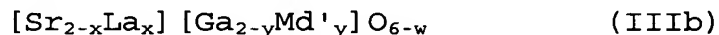
x and y are greater than or equal to 0 and less than or equal to 2 and w is such that the structure in question is electrically neutral.

20. The composite as defined in claim 19, in which compound (C₁) is of formula (IIIa):

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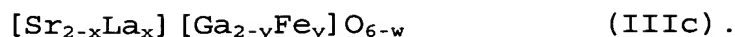


a compound of formula (IIIb):



and more particularly a compound of formula

(IIIc):



21. The composite as defined in claim 20, in which
5 compound (C₁) is of formula:
- $\text{Sr}_{1.4}\text{La}_{0.6}\text{GaFeO}_{5.3};$
 $\text{Sr}_{1.6}\text{La}_{0.4}\text{Ga}_{1.2}\text{Fe}_{0.8}\text{O}_{5.3};$
 $\text{Sr}_{1.6}\text{La}_{0.4}\text{GaFeO}_{5.2};$
 $\text{Sr}_{1.6}\text{La}_{0.4}\text{Ga}_{0.8}\text{Fe}_{1.2}\text{O}_{5.2};$
10 $\text{Sr}_{1.6}\text{La}_{0.4}\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_{5.2};$
 $\text{Sr}_{1.6}\text{La}_{0.4}\text{Ga}_{0.4}\text{Fe}_{1.6}\text{O}_{5.2};$
 $\text{Sr}_{1.6}\text{La}_{0.4}\text{Ga}_{0.2}\text{Fe}_{1.8}\text{O}_{5.2};$
 $\text{Sr}_{1.6}\text{La}_{0.4}\text{Fe}_2\text{O}_{5.2};$
 $\text{Sr}_{1.7}\text{La}_{0.3}\text{GaFeO}_{5.15};$
15 $\text{Sr}_{1.7}\text{La}_{0.3}\text{Ga}_{0.8}\text{Fe}_{1.2}\text{O}_{5.15};$
 $\text{Sr}_{1.7}\text{La}_{0.3}\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_{5.15};$
 $\text{Sr}_{1.7}\text{La}_{0.3}\text{Ga}_{0.4}\text{Fe}_{1.6}\text{O}_{5.15};$
 $\text{Sr}_{1.7}\text{La}_{0.3}\text{Ga}_{0.2}\text{Fe}_{1.8}\text{O}_{5.15};$
 $\text{Sr}_{1.8}\text{La}_{0.2}\text{GaFeO}_{5.1};$
20 $\text{Sr}_{1.8}\text{La}_{0.2}\text{Ga}_{0.4}\text{Fe}_{1.6}\text{O}_{5.1};$ or
 $\text{Sr}_{1.8}\text{La}_{0.2}\text{Ga}_{0.2}\text{Fe}_{1.8}\text{O}_{5.1}.$
22. The composite as defined in either of claims 7 and
17, in which compound (C₁) is chosen from compounds
25 of formula:
- $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Ga}_{0.1}\text{O}_{3-\delta}$ or
 $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta},$
- and compound (C₂) is chosen from magnesium oxide
(MgO), aluminum oxide (Al₂O₃), mixed strontium
30 aluminum oxide Sr₃Al₂O₆ and mixed barium titanium
oxide (BaTiO₃).
23. The composite as defined in claim 22, which
comprises between 2 and 10 vol% magnesium oxide
35 (MgO) and between 90 and 98 vol% La_{0.6} Sr_{0.4} Fe_{0.9}
Ga_{0.1} O_{3-δ}.
24. A method of preparing the composite as defined in
one of claims 1 to 23, characterized in that it

includes at least one step of sintering a powder blend of compound (C_1) and compound (C_2), while controlling the oxygen partial pressure (pO_2) of the gaseous atmosphere surrounding the reaction mixture.

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25. The method as defined in claim 23, in which the sintering step is carried out in a gaseous atmosphere having an oxygen partial pressure of 0.1 Pa or less.
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26. The method as defined in either of claims 24 and 25, in which the powder blend of compound (C_1) and compound (C_2) undergoes, before the sintering step, a forming step followed by binder removal.
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27. The use of the composite as defined in one of claims 1 to 23 as a mixed conducting composite for a catalytic membrane reactor, intended to be used for the synthesis of syngas by catalytic oxidation of methane or natural gas and/or as mixed conducting composite for a ceramic membrane intended to be used for separating oxygen from air.
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28. A method for inhibiting and/or controlling the crystal growth of the grains of mixed electronic/oxide ionic conducting compounds during the sintering step in the preparation of a catalytic membrane reactor, characterized in that it includes a prior step of blending 75 to 99.99 vol% of mixed conductor (C_1) with 0.01 to 25 vol% of compound (C_2).
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29. The method as defined in claim 28, comprising between 2 and 10 vol% magnesium oxide (MgO) and between 90 and 98 vol% $La_{0.6}Sr_{0.4}Fe_{0.9}Ga_{0.1}O_{3-\delta}$.
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